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MOLECULAR PROCESSES IN A HIGH TEMPERATURE SHOCK LAYER

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This is the third semi-annual progress report describing research on molecular processes in a high temperature shock layer.

I. Introduction

In previous semi-annual progress reports, I have described the development of techniques for the calculation of electron capture widths, electronic wave functions, cross sections and rates needed for the description of the dissociative recombination (DR) of molecular ions with electrons. The cross sections and rates have been calculated by using harmonic oscillator wave functions for the ion and a delta function approximation for the continuum vibrational wave function in the repulsive dissociative channel. In order to obtain DR cross sections of quantitative accuracy, a computer program which solves the one dimensional nuclear motion wave equation has been revised to calculate the cross sections and rates. The program and the new results are described in section II. Included is a discussion of large windows found in the dissociative recombination cross sections from excited ion vibrational levels. These windows have not been previously reported in the literature.

The magnitude of the DR cross sections for several dissociative routes are sensitive to the location of the crossing of the neutral and ion potential curves. Section III describes studies of the effects of basis set and CI wave function size on vertical excitation energies. Preliminary studies on N_2 and O_2 using large scale wave functions are also reported.

II. Numerically Determined Rates and Cross Sections

The cross section, σ, for direct DR from ion vibrational level v is calculated from the following expression[1]:

$$\sigma_v = [2\pi r/k^2][\xi_v^2/(1+\sum_{v' \leq v}(\xi_{v'})^2)^2] \tag{1}$$

where k is the wave number of the electron, r is the ratio of the multiplicity
of the neutral state to that for the ion, and ξ_v is a matrix element over the
Hamiltonian operator of the electronic and nuclear wave functions in the
entrance and exit channels. Denoting the portion of the matrix element arising
from integration over electronic coordinates as V^{el}, we have

$$\xi_v = \pi < \chi_v \mid V^{el} \mid F_d > \tag{2}$$

where χ_v is the vibrational wave function of level v of the molecular ion and
F_d is the continuum vibrational wave function in the dissociative neutral
state. The electronic width is given by

$$\Gamma = 2\pi (V^{el})^2. \tag{3}$$

The electronic widths are calculated by methods described in previous
semi-annual reports. With the electronic widths and the vibrational wave
functions one can evaluate the cross sections from the expression in
(1). Previously, I have used harmonic oscillator wave function for the χ_v and
the delta function approximation for F_d. This approach ignores the effect of
potential curve anharmonicity on the vibrational wave functions and could lead
to cross sections of less than quantitative accuracy at low electron energies
for potential curves which cross the large R turning points of excited ion
vibrational levels. The delta function approximates the effect of the slope of
the dissociating neutral potential curve on the shape of the continuum
vibrational wave function and, as discussed below, leads to qualitatively
incorrect results for DR cross sections from excited ion vibrational levels. In

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order to obtain cross sections of quantitative accuracy I have revised a program which numerically determines the vibrational wave functions by solving the one dimensional nuclear Schroedinger equation. In order to obtain two figure accuracy in the calculated widths it is necessary to calculate the vibrational wavefunctions for the ion and the neutral state on a grid of $0.001a_O$. Each wave function is determined on a grid of 8000 points between $0.0a_O$ and $8.0a_O$. Cross sections have been calculated over a wide electron energy range from 0.001eV to 8.0eV and rates have been determined for electron temperatures between 100K and 30,000K. In order to cover this wide range over each of the lowest ten vibrational levels of the ion, a single large array of continuum vibrational levels is used for all ten ion vibrational levels. Cross sections up to 8 eV above each ion level on a grid of .00004h, i.e. 7350 cross sections are determined for each vibrational level. For O_2^+, this calculation requires a total of 9136 continuum wave functions. Since each of these 9136 wave functions is determined at 8000 points a total of about 73×10^6 continuum wave function amplitudes are calculated in a single run of the program. For each vibrational level, the 7350 matrix elements given in (2) are calculated by Simpson's rule and the cross sections are determined from (1). The denominator on the right side of (1) accounts for autoionization and is included by summing over the appropriate matrix elements in the 7350 length arrays for the lower vibrational levels. From the cross sections, the rates are obtained by numerical integration assuming a Maxwellian distribution of electron energies. A single run of the program which obtains both cross sections and rates for the lowest ten vibrational levels of O_2^+ over the electron energy and temperature ranges given here takes about 8 minutes on the NASA Ames Cray X-MP computer.

Fig.s 1-10 present the numerically determined cross sections for DR of the $^1\Sigma_u^+$ state of O_2^+ and are based on wave functions determined in the [5s,4p,1d] basis described in the next section. At low electron energies the numerically

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determined cross sections from v=0 are about a factor of 3 larger than the harmonic oscillator cross sections determined previously[2]. The qualitative shape of the cross section from v=0 is similar to that obtained previously with the harmonic oscillator wave functions. The maximum near 3eV is characteristic of a large R crossing of dissociative and neutral curves[2] as is the case here for $^1\Sigma_u^+$ which crosses the ion between v=1 and v=2. The maximum reflects the shape of the v=0 vibrational wave function of the ion. Small breaks in the cross section above 0.25 eV are due to autoionization.

Fig. 2 shows a large window near 2.5 eV in the DR cross section from v=1. The window is due to the single node in the v=1 wave function. At the appropriate energy the numerator in Eq.(1) decreases due to decreasing overlap between the vibrational wave functions. It is important to note that while large windows occur in all the cross sections from excited vibrational states, none of the cross sections vanish, i.e. the numerator in Eq.(1) is always greater than zero. If the delta function had been used to approximate the continuum vibrational wave functions the cross sections would vanish at the windows.

Since ion vibrational level v has v nodes, one would expect the number of windows to increase with increasing v. Fig.s 1-10 show that for v≤3 cross sections from the vth level have v windows, for v=4 there are three windows, v=5,6,and 7 have 4 windows, and v=8 and 9 have 5 windows. Note that the delta function approximation would yield v windows for the vth vibrational level.

The DR rates are given in Fig.s 11 and 12. The v=2 rate is the highest and is nearly two orders of magnitude higher than the v=0 rate. As a result, vibrational excitation of the ion will be very important in determining the total rate for $O(^1S)$ production.

It has been customary in the atmospheric modelling literature to guess the rate for production of $O(^1S)$ by multiplying the laboratory rate for total DR by a small fraction derived from the laboratory results of Zipf[3]. (The laboratory

experiments are quite difficult and their interpretation is plagued by uncertainties in the electron and vibrational temperatures and the role of $O(^1S)$ excitation due to collision of ground state O with metastable Ar. The current situation is such that there are no reliable laboratory derived rates for ^1S production by DR.) Even if the fraction of $O(^1S)$ arising from DR is known at one temperature this procedure is incorrect since the electron temperature dependence for producing excited O varies with ion vibrational level. The results obtained here show that at low electron temperatures for v=0 the rate varies as $T_e^{-0.35}$, and for v=1,2, and 3 it varies as $T_e^{-0.40}$, $T_e^{-0.44}$, and $T_e^{-0.58}$, respectively. For a non-Boltzmann distribution of ion vibrational levels, as is expected in the upper atmosphere, the total rate can be constructed from the rates in Fig.s 11 and 12.

The rates as a function of a Boltzmann vibrational temperature are shown in Fig. 13. As expected, at 300K the rate is dominated by the v=0 rate and varies as $T_e^{-0.35}$.

III Large Basis Set Electronic Wave Functions

The full first order (FFO) wave functions used previously[*] for DR studies had about 2000 terms in the CI expansions. Larger wave functions having all single and double excitations (CISD) from a multireference set of configurations have been studied in the current reporting period. Using the same double zeta plus polarization basis set reported previously for the first order wave functions, the CISD wave functions (having about 13,000 terms) gave potential curves which were quite similar to the first order curves. Calculations on the excited $^1\Sigma_u^+$ curve of O_2 gave a vertical excitaion energy of 12.63 eV compared to 12.73eV for the first order wave function. The similarity in shape of the first order and CISD potential curves indicated that it would be worth while to investigate larger basis sets. The CISD calculations

were then repeated with a [5s,4p,1d] Gaussian basis set[5]. Several studies were carried out including an analysis of the importance of constructing excited state CI wave functions from orbitals optimized for the excited state and optimized for the ground state. Also, the importance of the quadruples correction[6] to the CISD energy was studied. In general, the correction to the vertical excitation energy for missing quadruples is quite important when ground state orbitals are used in both the ground and excited states. However, the correction decreases to about 0.38 eV if excited state optimized MCSCF orbitals are used in the upper state. In the latter case, the correction for missing quadruples is small for the excited state energy (0.08eV) but large for the ground state (0.46eV). The vertical excitation energy for $^1\Sigma_u^+$ above the calculated ground state minimum is 12.89eV for the quadruply corrected (CISDQ) multireference wave function compared to the smaller basis results of 12.73eV for the FFO wave function and 12.63eV for CISD. Considering that these wave functions range in size from 50,000 to 2,000 terms the difference in excitation energies is quite small. There are no experimentally derived excitation energies for the $^1\Sigma_u^+$ state. However, by fitting a potential curve and dipole moment function to experimentally determined cross sections for excitation of the $^3\Sigma_u^-$ state of O_2 a vertical excitation energy of 8.62eV has been obtained[7]. The CISDQ vertical excitation energy for the case where optimized MCSCF excited state orbitals are used for the upper state is 8.47eV indicating that this approach can place the low lying excited states relative to the ion to about 0.15 eV accuracy. Experimentally derived vertical excitation energies to higher valence states of O_2 are not known.

With the use of Complete Active Space Self Consistent Field (CASSCF) and the direct CI codes implemented in the set of SWEDEN[8] programs on the NASA Ames Cray I have begun studies of larger scale wave functions for both N_2 and O_2. Contracted Gaussian basis sets of [6s,4p,2d,1f] size have been constructed from the [5s,3p] contraction of Dunning supplemented with the most diffuse

primitives listed by Salez and Veillard[9]. Two primitive sets of 3d polarization functions with exponents 1.8847 and .55826 and a 4f primitive set with an exponent of 1.2 were included in the basis set. After several tests, it was found that the [5s,3p] contractions recommended by Salez and Veillard are slightly over contracted for N and excessively over contracted for O in the valence region. For example, using the recommended [5s,3p] set of Salez and Veillard for O and supplementing these functions in an analogous manner to that recommended for N_2 by Langhoff, Bauschlicher and Chong[10] leads to a [6s,4p,3d,1f] basis with a Hartree Fock (HF) energy of -149.647247h at R=2.2819 compared to -149.651826h for the much smaller [5s,4p,1d] basis described earlier! The [6s,4p,2d,1f] basis derived here gives a HF energy of -149.660085h and is quite close to the HF limit of -149.6639[11]. A [6s,4p,2d,1f] basis derived in the same manner for N_2 gives a HF energy of -108.987719h at R=2.07432 and is similar to the result of -108.985764 reported by Langhoff, Bauschlicher and Chong[10] in a [6s,4p,3d,1f] basis derived from a Salez-Veillard contraction supplemented with polarization and diffuse functions.

For the [6s,4p,2d,1f] basis derived here for N_2 a CASSCF wave function with the 2p space active has been used for orbital determination. A CISD from a multireference set for the ground state yields a 52333 term wave function with a potential curve having a fundamental frequency of $2393.73cm^{-1}$ and an equilibrium separation of $2.0756a_0$ compared to the experimental values of $2358.56cm^{-1}$ and $2.074347a_0$. With the correction for missing quadruples the results are $2349.89cm^{-1}$ and $2.0831a_0$. These results are quite encouraging and calculations are now proceeding to determine the important dissociative routes of N_2 and other important routes for O_2.

IV. References

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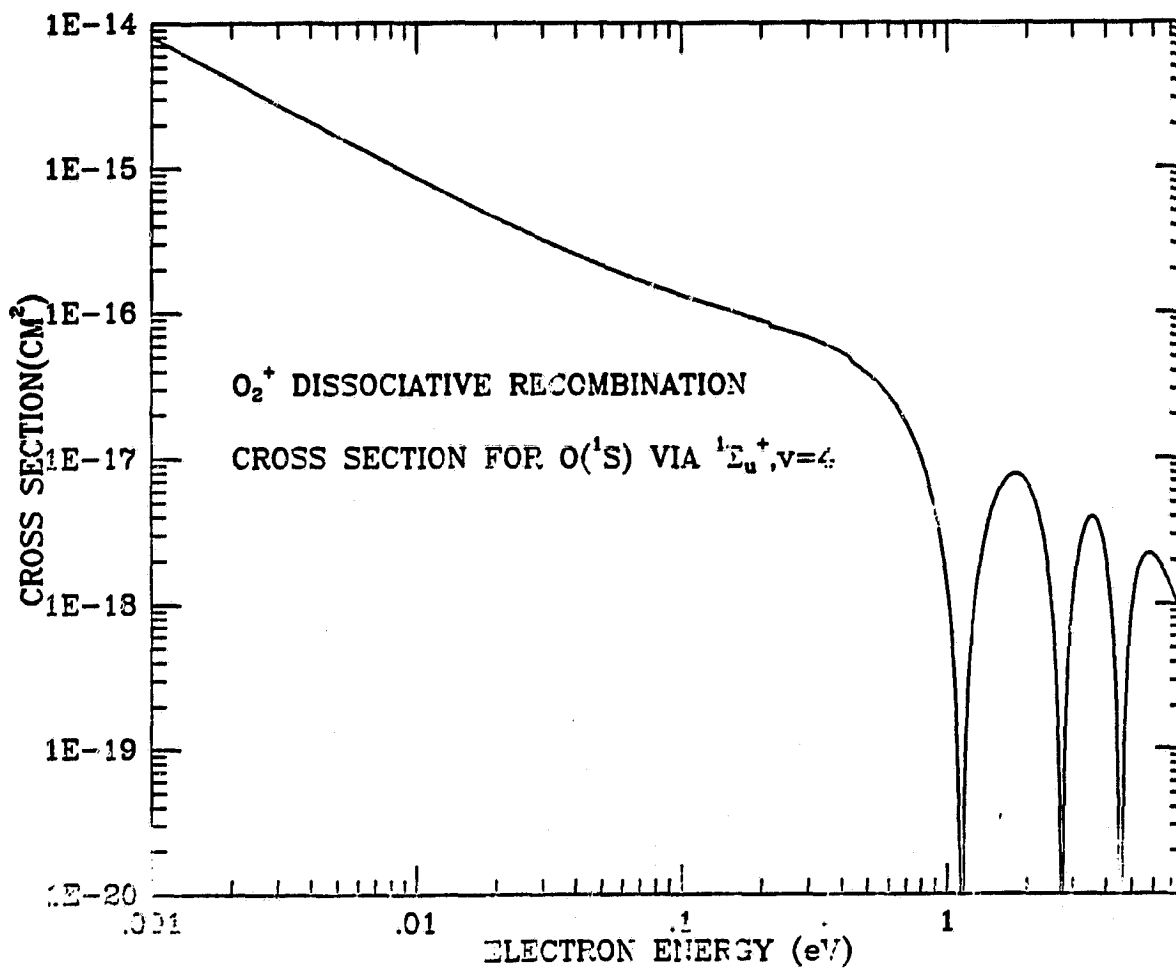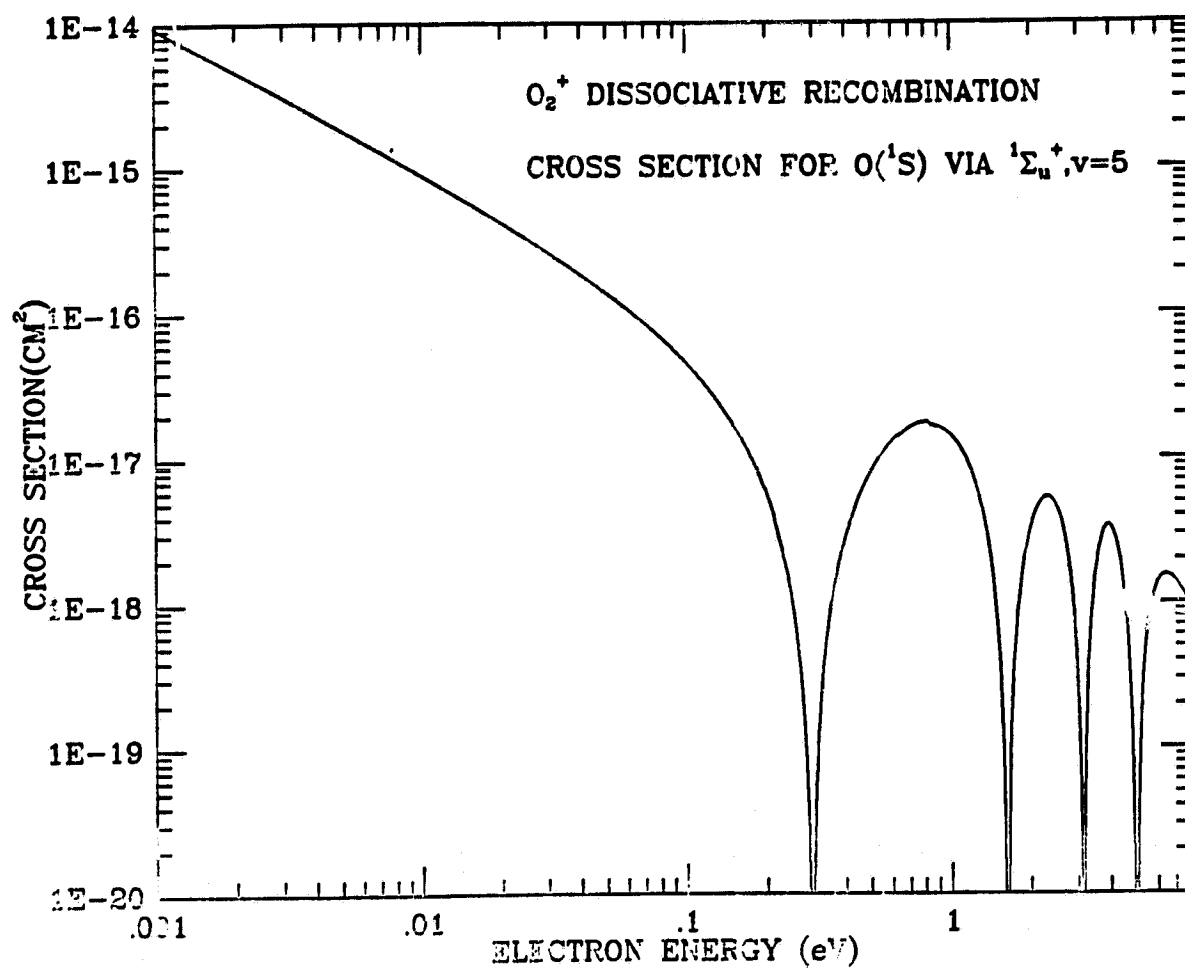11. P. E. Cade, unpublished results (see H. Schaefer, J. Chem. Phys. 54, 2207(1971).
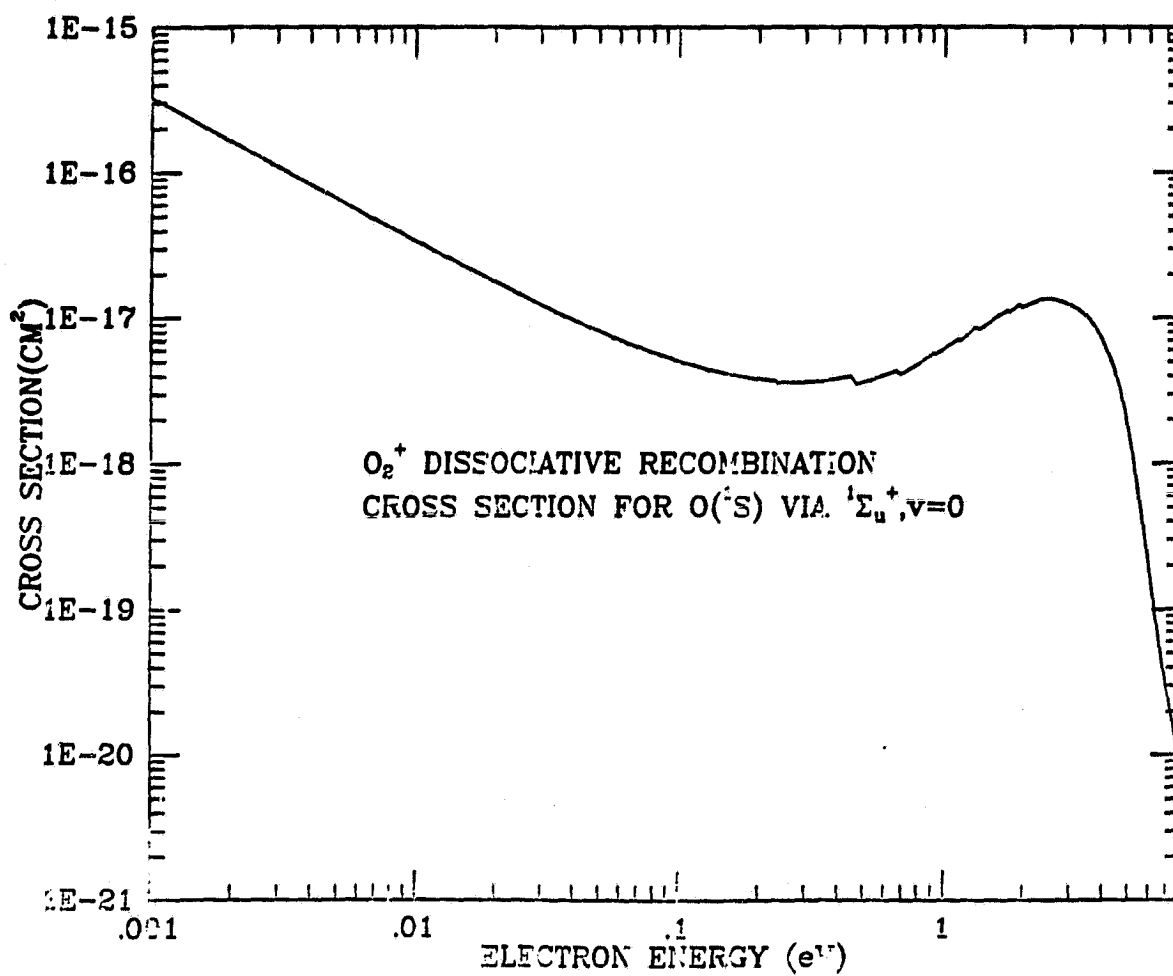
Fig. 1. DR cross section for the v=0 ion
vibrational level.
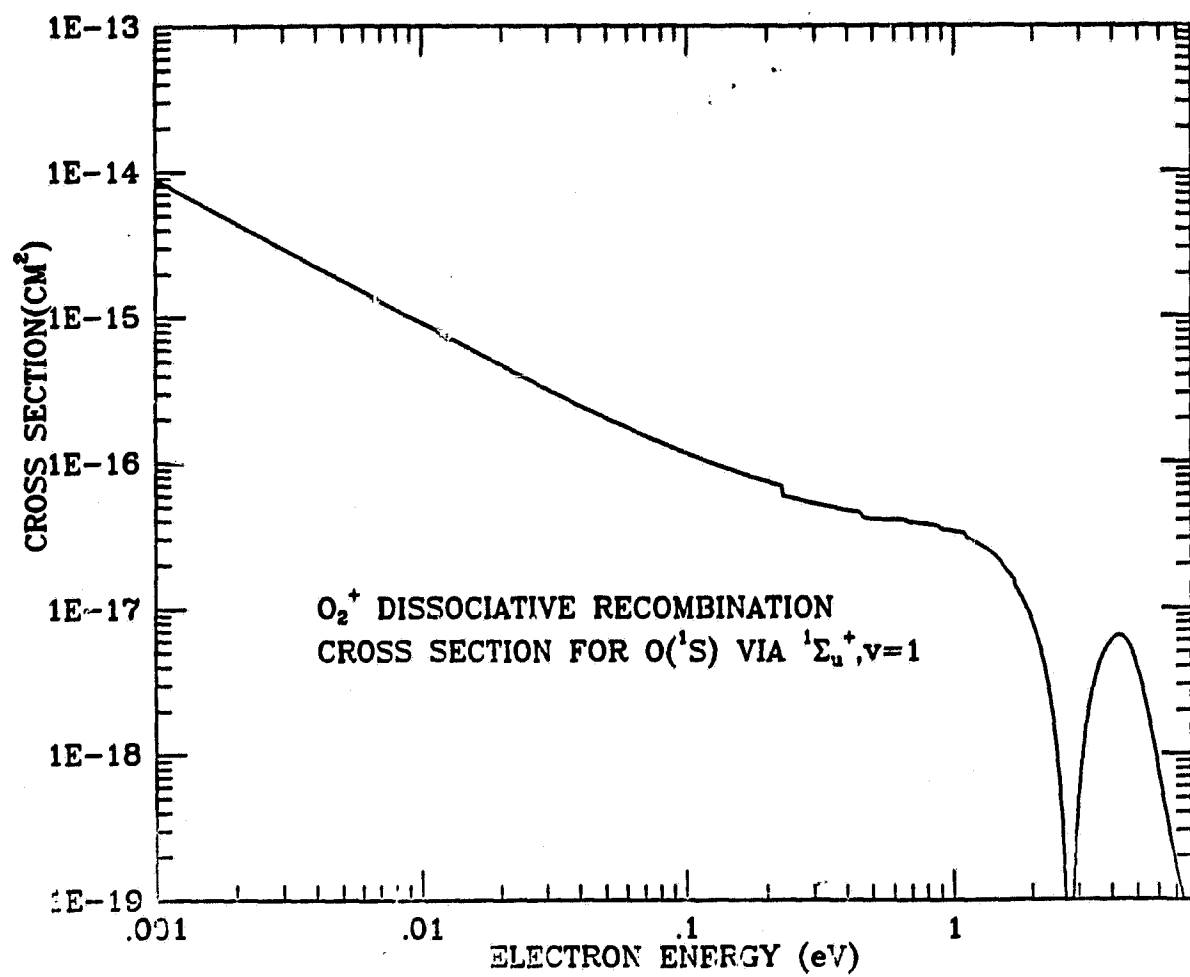
Fig. 2. DR cross section for the v=1 ion
vibrational level.
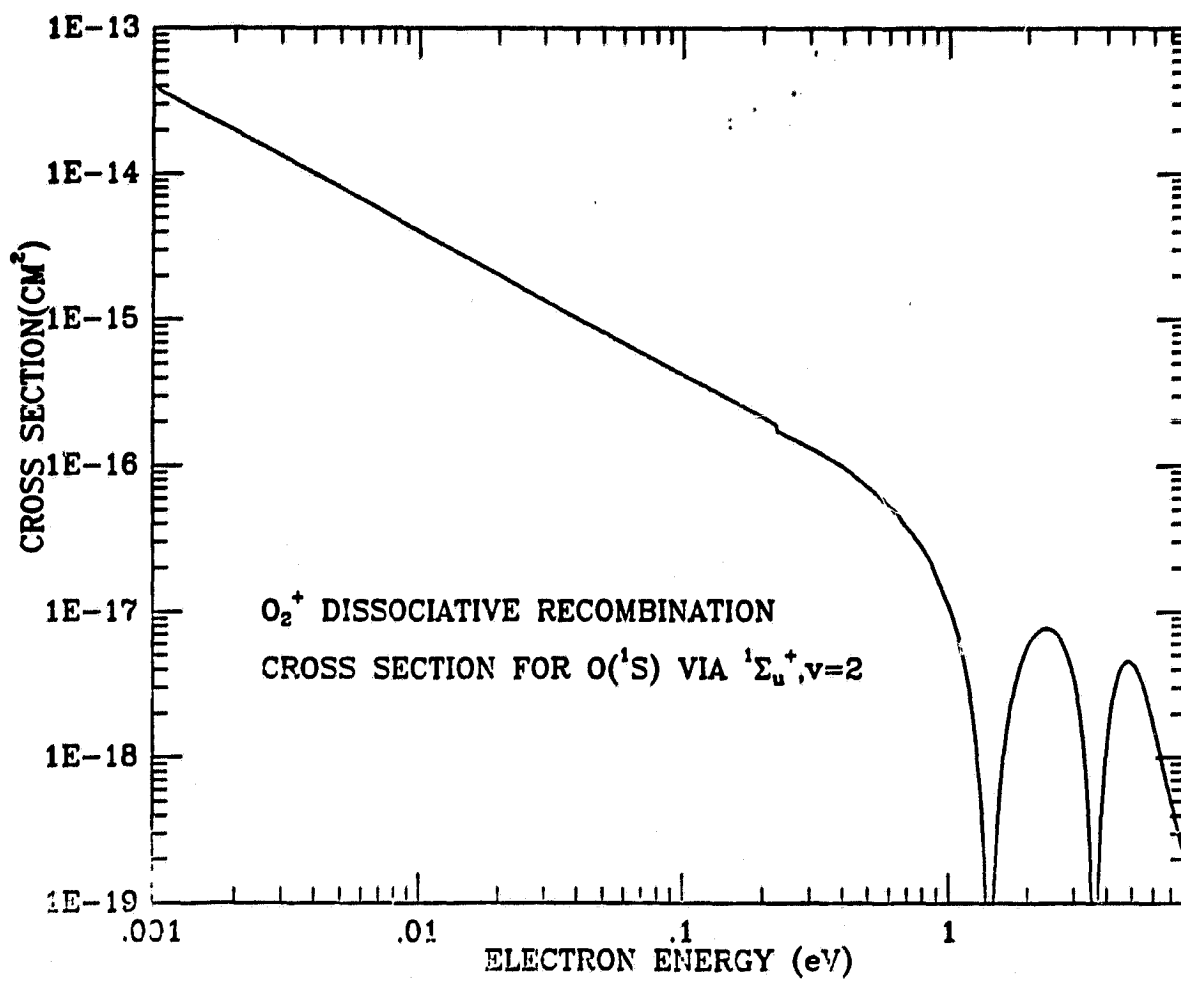
Fig. 3. DR cross section for the v=2 ion
vibrational level.
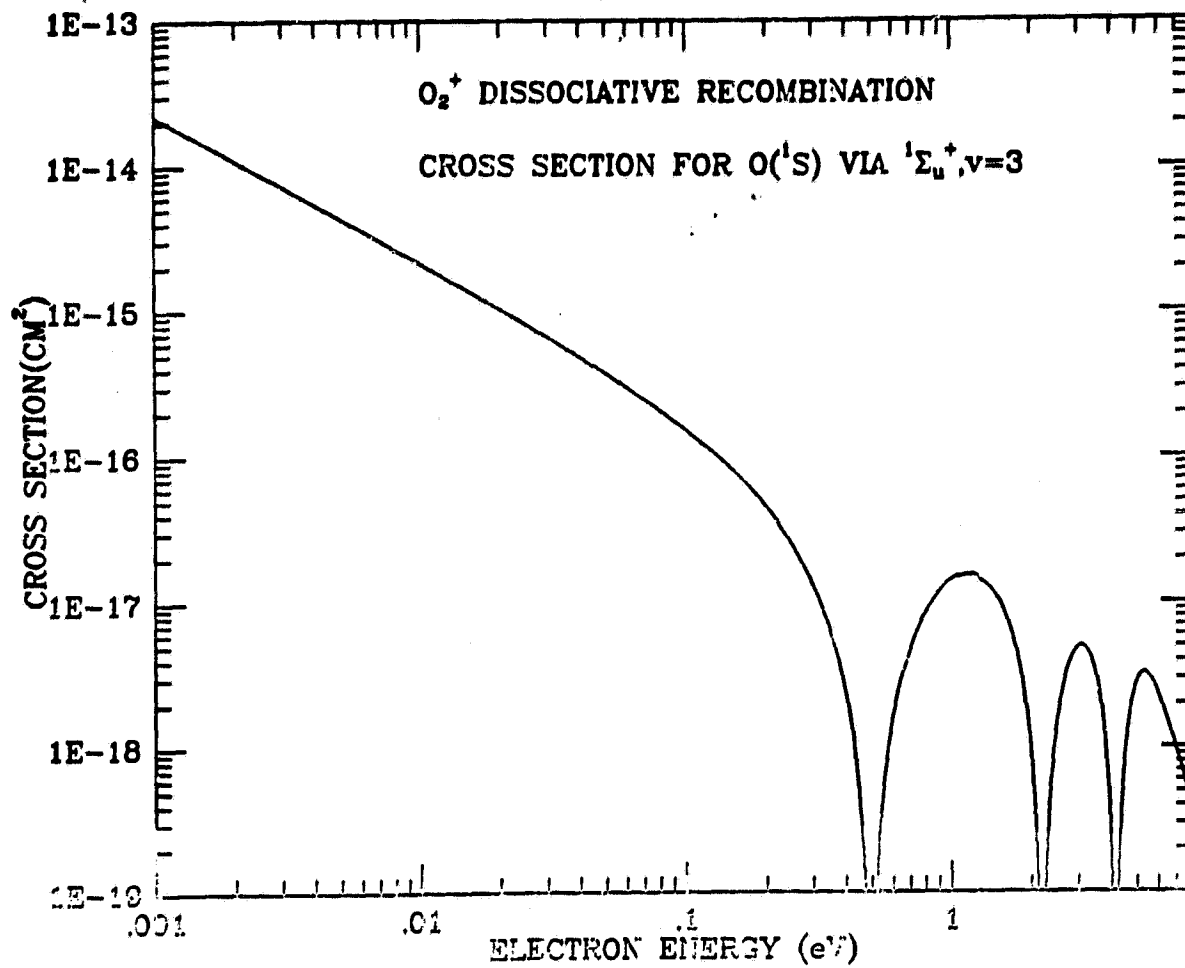
Fig. 4. DR cross section for the v=3 ion
vibrational level.

Fig. 5. DR cross section for the v=4 ion
vibrational level.

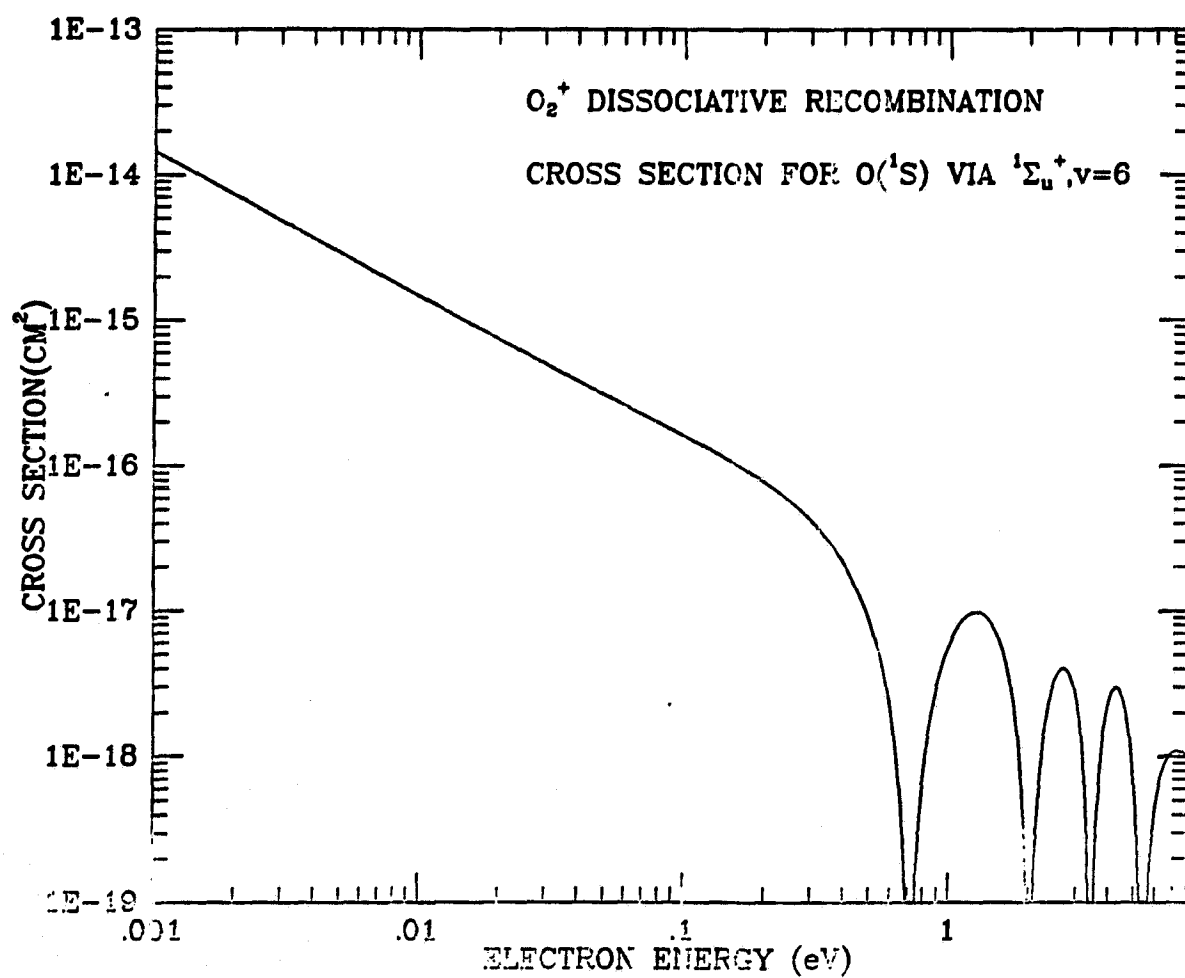Fig. 6.   DR cross section for the v=5 ion
          vibrational level.

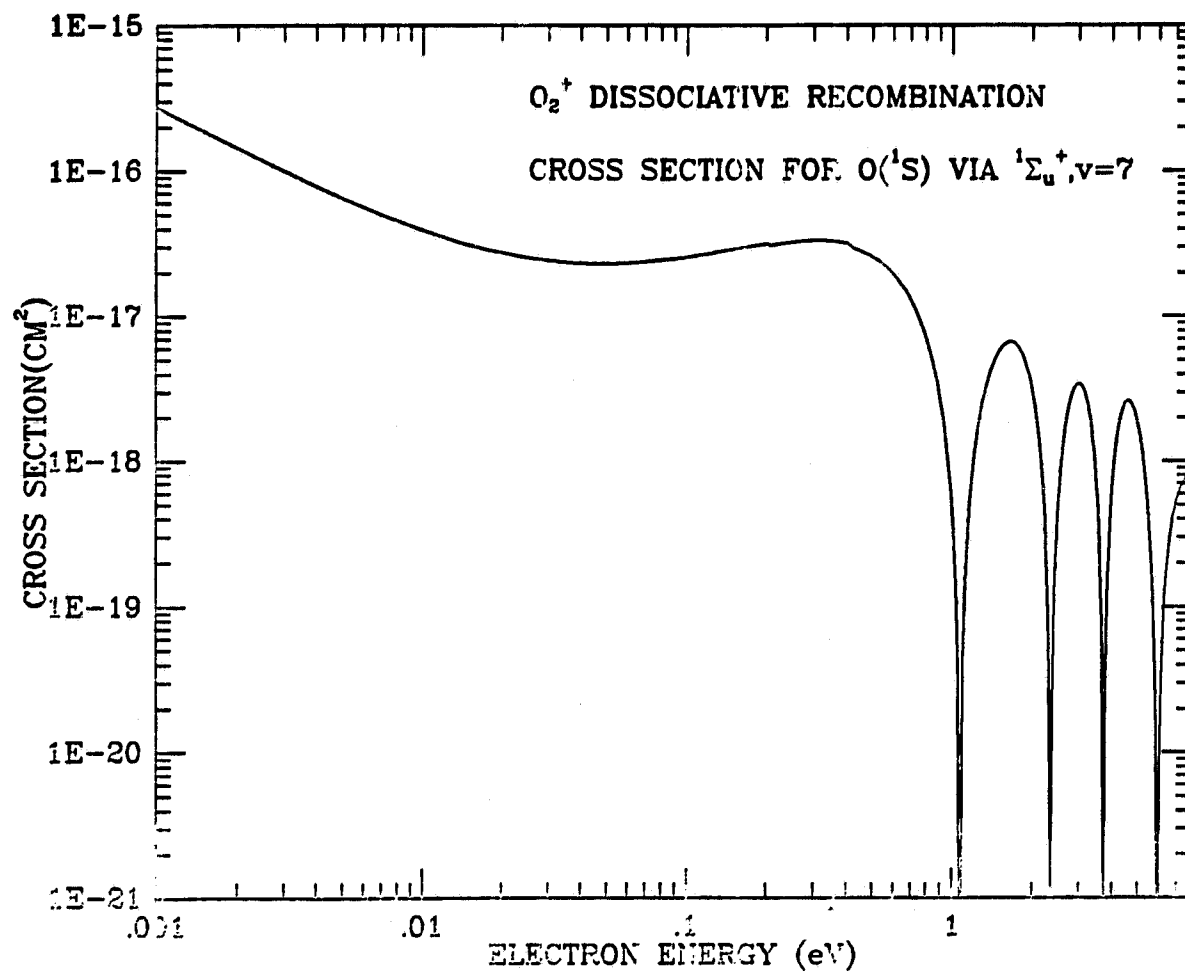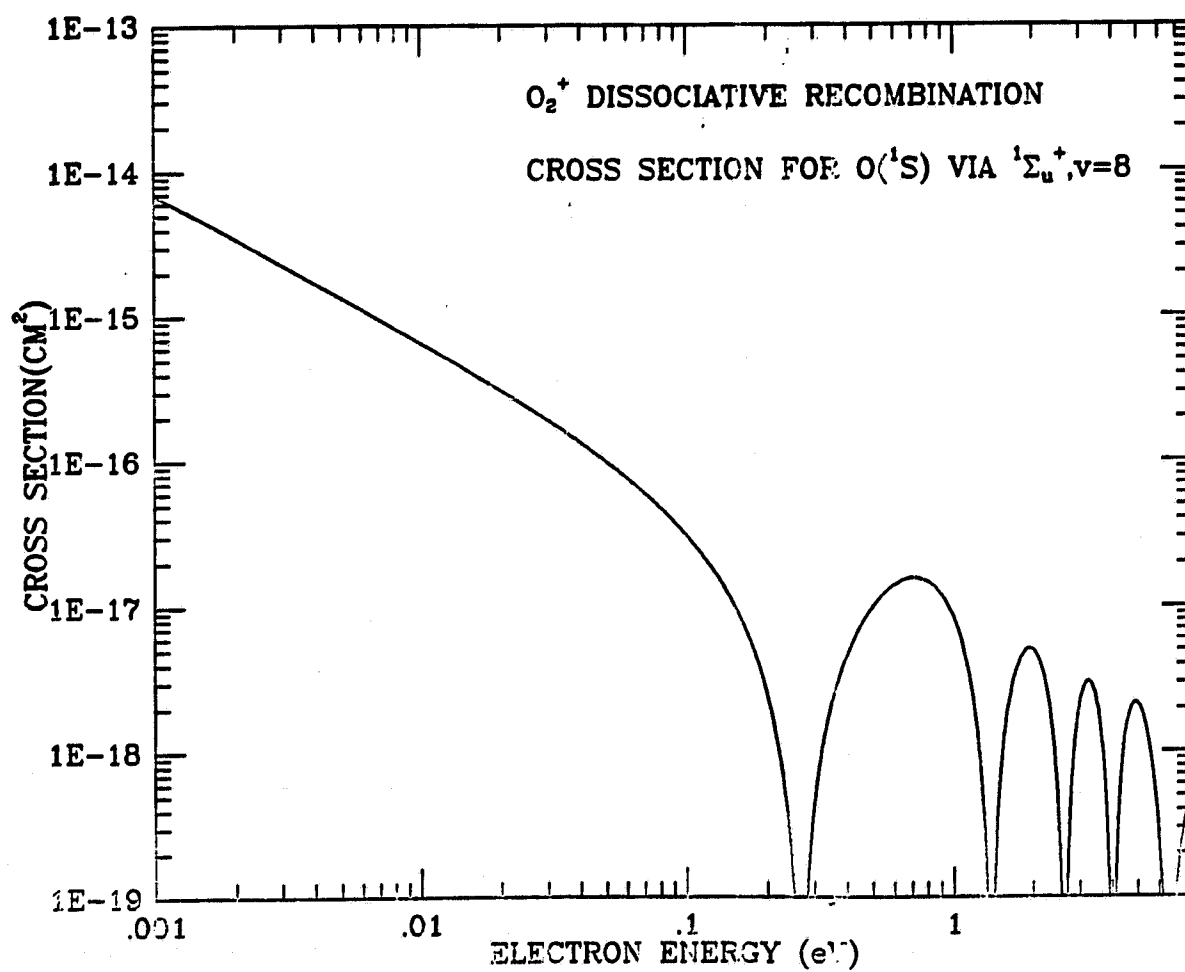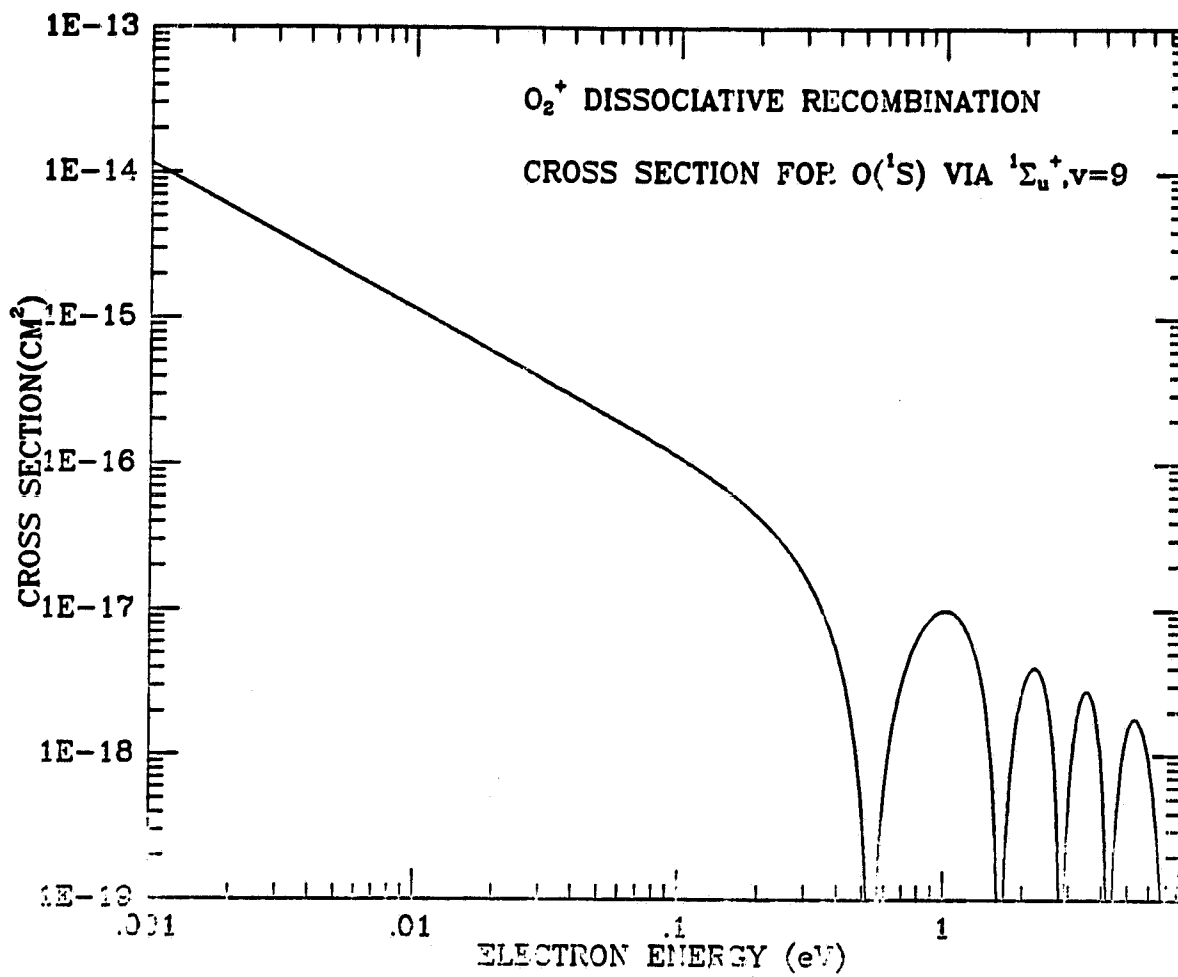Fig. 7. DR cross section for the v=6 ion
vibrational level.

Fig. 8.   DR cross section for the v=7 ion
          vibrational level.

Fig. 9. DR cross section for the v=8 ion
vibrational level.

Fig. 10. DR cross section for the v=9 ion
vibrational level.
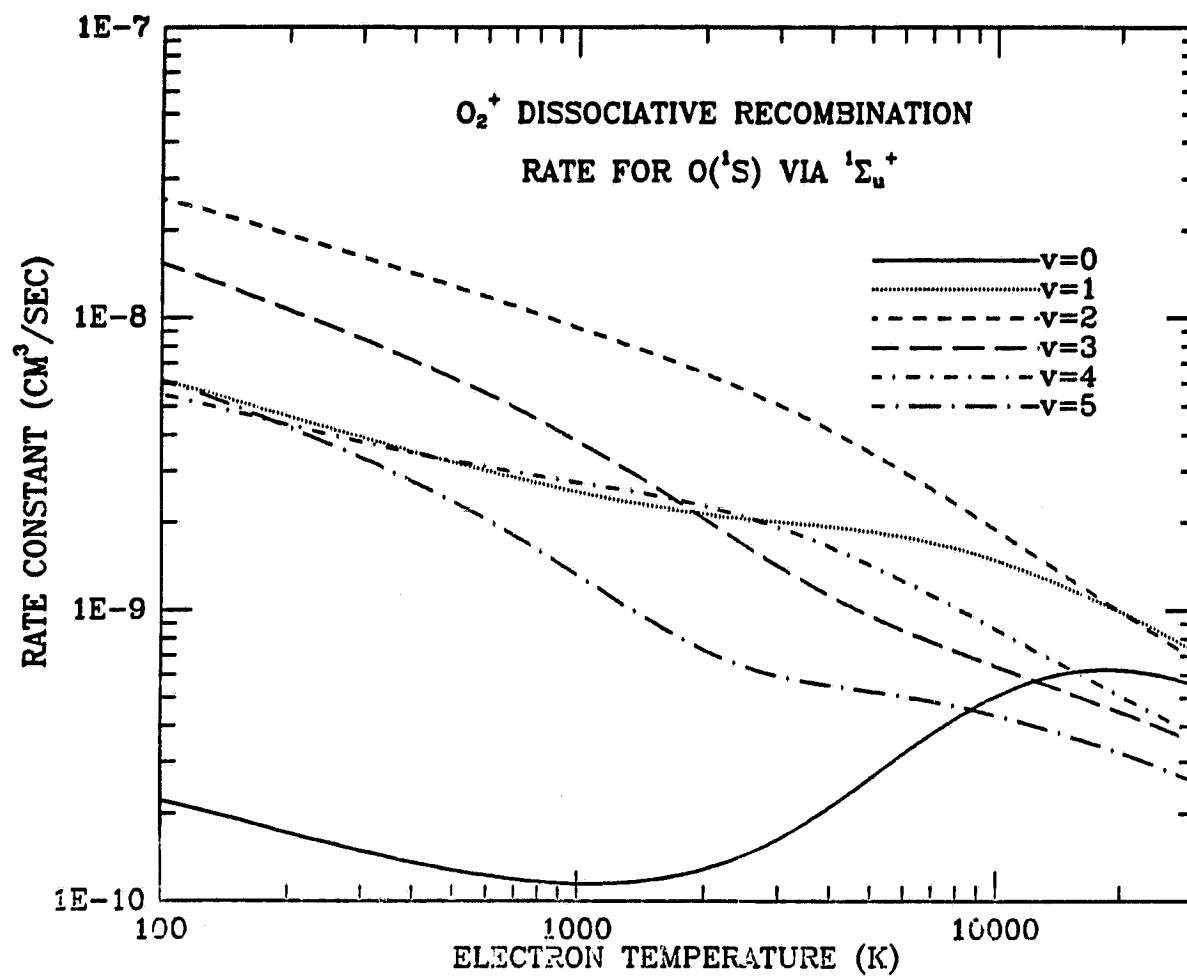
Fig. 11. DR rate for the v=0-5 vibrational
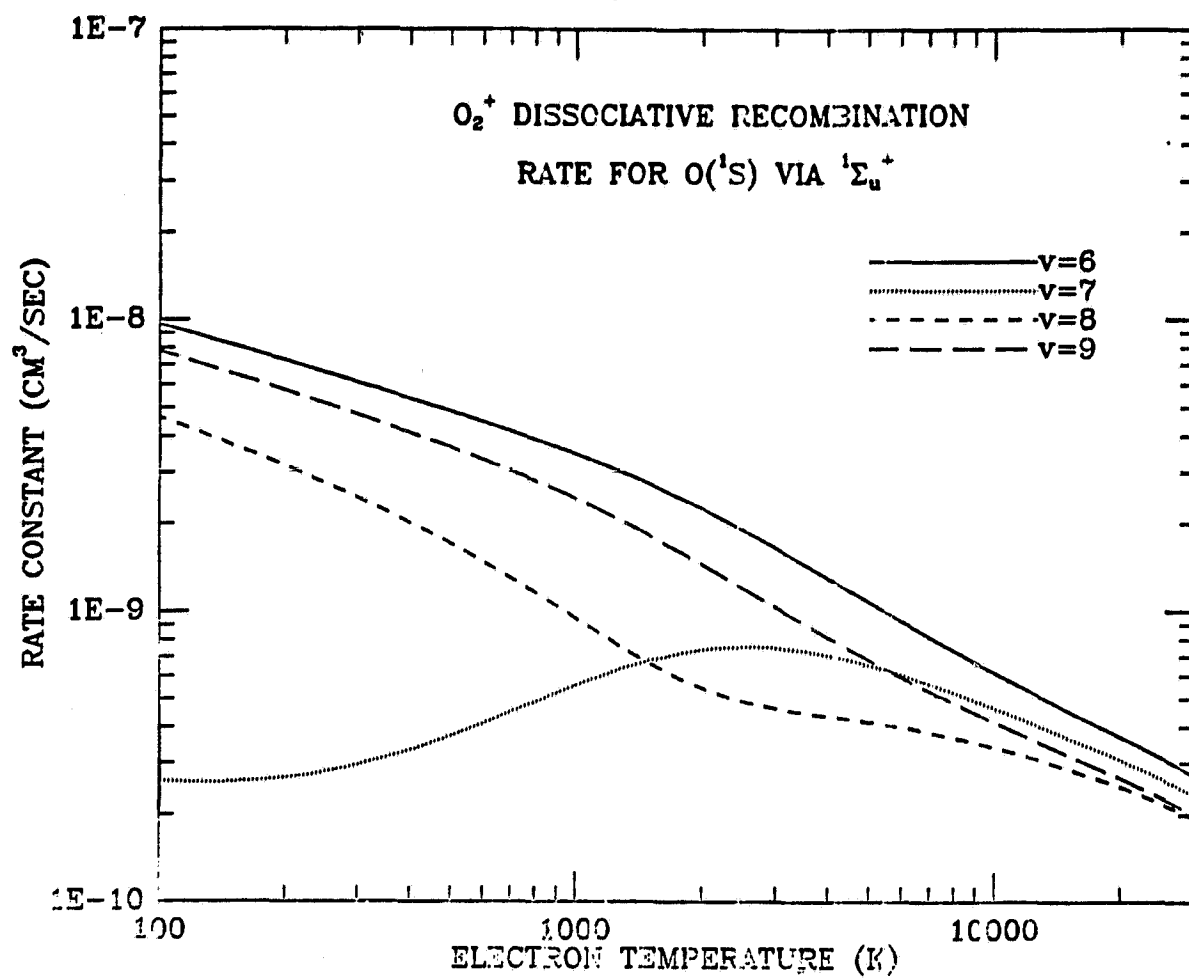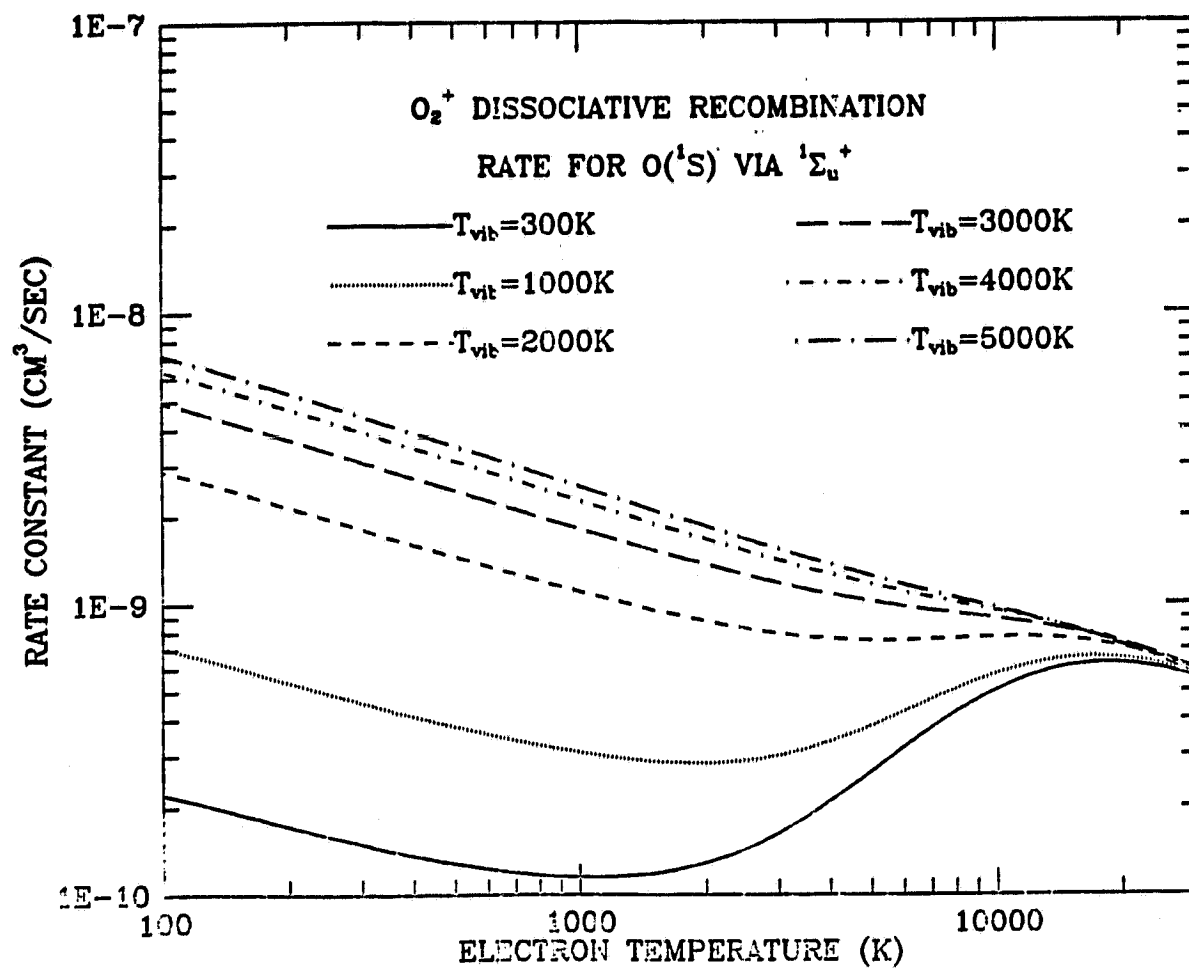levels of the ion.

Fig. 12. DR rate for the v=6-9 vibrational
levels of the ion.

Fig. 13.   DR rates for six ion vibrational
temperatures.